

# Mechanisms of damage by salt

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**Abstract:** Limestone is very susceptible to the aggressive action of salts. This paper describes the current understanding of the mechanisms by which salt crystallization causes damage to limestone. Crystallization pressure increases with the supersaturation of the solution, which may result from rapid drying and/or decrease in temperature. Salts with a tendency to achieve higher supersaturation owing to a high nucleation barrier are potentially able to induce more severe damage. In the presence of small pores (<100 nm), equilibrium thermodynamics indicates that crystallization pressure can result from the curvature dependence of the solubility of a salt crystal. Under non-equilibrium conditions, high transient stresses can occur even in larger pores. In the field, the complexity of salt weathering results from heat, moisture and ion transport coupled with in-pore crystallization during changing climatic conditions. This paper describes how progress in the modelling and numerical simulation of these coupled processes can contribute to a better understanding of the influencing factors and assessment of critical conditions.

Classically, tests such as the bursting test and the capillary rise experiment with simultaneous evaporation have been applied to evaluate qualitatively stone deterioration induced by salt crystallization. More recently our group has introduced other experimental methods to the field of salt weathering that provide quantitative information about nucleation and crystallization kinetics in porous materials (by differential scanning calorimetry), induced deformation and stress (by dynamic mechanical analysis and a novel warping test), and pore clogging caused by in-pore crystallization.

The final part of this paper is dedicated to a discussion of methods to prevent damage that may alter one of the crystallization steps, such as nucleation, crystal growth, disjoining pressure between mineral and crystal surfaces, or solution properties. Indeed, efficient treatments have been found for particular scenarios in the laboratory; however, the consequences of these treatments in the field, such as the behaviour at other temperatures and concentrations as well as the durability of the treatments, are not known yet.

Indeed, a lack of knowledge still exists in understanding the pore-level crystallization, such as the processes in the thin film between mineral surfaces and salt crystals that determine the disjoining pressure, or the dynamics of crystallization within the pore network that influence the salt distribution and stress in the stone. Atomic force microscopy, surface force measurements, nuclear magnetic resonance and simulations using molecular dynamics are promising methods to elucidate these points. By understanding these remaining questions a more reliable protection of stone against salt weathering will be achieved.

Limestone is very common in architecture, especially in North America and Europe. It was a very popular building block in the Middle Ages because it is hard, durable and easily accessible at surface exposures. Many medieval churches and castles in Europe are made of limestone, as are landmarks across the world, including the pyramids in Egypt. The longevity of such monuments is threatened by the same processes that sculpt natural landforms (Goudie & Viles 1997), prominent among which is the stress exerted by salts crystallizing in the pores of the stone (Chatterji & Jensen 1989; Flatt 2002).

Salts that are found in the pores of limestone are mainly absorbed with groundwater, result

from reaction with atmospheric pollutants (such as sulphates in industrial regions), are transported with the air (such as chloride salts in coastal areas) or are supplied to the building by de-icing salts.

Salts originating from air pollutants affect many monuments, such as the Al-hambra, an immense and valuable archaeological site in Granada, and churches in northern parts of the UK made from dolomitic limestone and suffering the consequences of the coal-burning power plants formerly located in this area. The photographs in Figure 1 show severe efflorescence of magnesium sulphate salts (left) and flaking resulting from subflorescence of the same salt in the dolomitic limestone (right) used in Howden Minster, Yorkshire, UK.

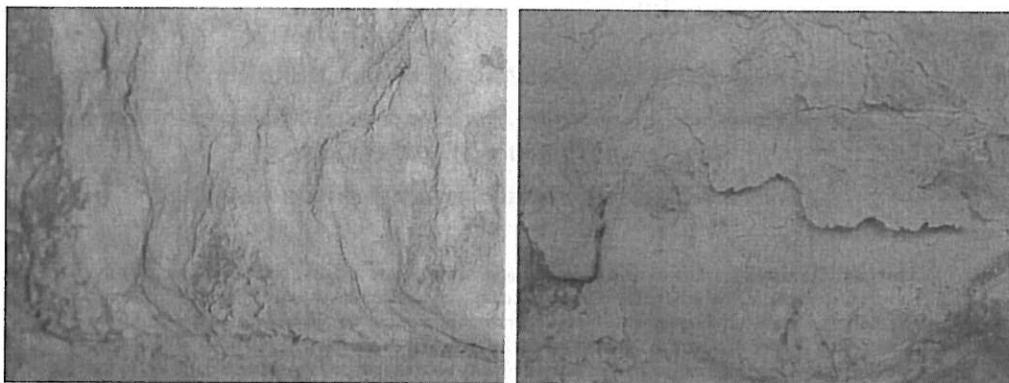


Fig. 1. Efflorescences of magnesium sulphate salts (left) and flaking (right) of the dolomitic limestone in Howden Minister, UK.

Salt-induced deterioration of architectural heritage and of geological, or geo-archaeological, sites is accelerated drastically in marine environments, such as the Mediterranean Basin. Rothert *et al.* (2007) reported on the intense damage caused by the action of salt crystallization in monuments and buildings constructed of the local Globigerina Limestone in the Maltese Islands. Similar observations are presented about sites in Alexandria, mainly built from oolitic limestone blocks (Ibrahim & Kahm 2005), sites on the SW coast of France (Cardell *et al.* 2003) and Roman monuments in Tarragona (Vendrell-Saz *et al.* 1996).

A great effort has been made in recent decades to understand the damage mechanisms responsible for salt weathering (e.g. Chatterji & Jensen 1989; Rodriguez-Navarro & Doehne 1999; Scherer 1999, 2004; Rodriguez-Navarro *et al.* 2000a; Flatt 2002; Steiger 2005a, b; Espinosa-Marzal & Scherer 2008a; Steiger & Asmussen 2008), as well as to develop methods to prevent damage (e.g. Rodriguez-Navarro *et al.* 2000b, 2002; Houck & Scherer 2006; Lubelli & van Heess 2007; Ruiz-Agudo & Rodriguez-Navarro 2010). Indeed, the application of new protective treatments and consolidants to protect stone against weathering is an important issue worldwide (Delgado Rodrigues & Manuel Mimoso 2008).

There have been several reviews on salt damage in recent years concerning the understanding of salt crystallization in porous materials, the damage mechanisms and the major influencing factors, such as the supersaturation and the porosity (Goudie & Viles 1997; Charola 2000; Doehne 2002; Charola *et al.* 2006). This paper complements those reviews with recently introduced experimental methods, advances in the modelling and numerical simulation of salt weathering, and new directions in the prevention of salt damage, and points out possible directions for future research.

### Salt crystallization and damage mechanisms

In this section we give an overview of the main factors influencing salt crystallization and damage of stone. Supersaturation is the driving force for crystallization, which leads to crystallization pressure and damage, even in the absence of small pores. The significance of the interaction between in-pore crystallization and moisture/salt transport, including pore clogging, is emphasized. The consequences of these interactions (in particular for favouring or preventing damage) are not well understood, so further study is necessary. The currently available computational power permits simulations of the coupled processes on both laboratory and field scales, which promises to advance our understanding of complex interactions, including changing climatic conditions, the behaviour of salt mixtures and the effectiveness of poultices, among others. The end of this section deals with the stress induced by the crystallization pressure, which is a decisive topic in terms of predicting durability of stone. Very recently, there have been a few attempts to predict damage.

### Supersaturation – nucleation and crystal growth

A good background on the theory of heterogeneous nucleation and crystal growth can be found in Christian (1975), Nielsen (1984) and Mullin (1993), and, more recently, applied to salt crystallization in porous materials in Espinosa-Marzal & Scherer (2010a).

According to Gibbs' theory, supersaturation of the salt solution is thermodynamically necessary for nucleation (Mullin 1993). The driving force for crystallization is the difference between the

chemical potentials of solution and nuclei,  $\Delta\mu$ , which is related to the supersaturation,  $\beta$ , of the salt in the solution:

$$\frac{\Delta\mu}{RT} = \ln(\beta). \quad (1)$$

The supersaturation ratio is

$$\beta = \left(\frac{a_{\pm}}{a_{\pm}^*}\right)^{\nu} \cdot \left(\frac{a_w}{a_w^*}\right)^{\nu_0} \quad (2)$$

where  $a_{\pm}^*$  is the average ion activity of the saturated solution,  $\nu$  the ion mole number per mole of salt,  $R$  the gas constant,  $T$  the temperature,  $a_w$  the water activity,  $a_w^*$  the water activity in equilibrium, and  $\nu_0$  the number of water molecules per mole of salt (Steiger 2005a).

If the supersaturation ratio  $\beta$  is larger than 1, the solution is metastable and crystallization may begin or not. But when  $\beta$  is larger than a threshold value,  $\beta^* > 1$ , nucleation starts abruptly (Mullin 1993).

An energetic barrier for nucleation results from the fact that the formation of a critical nucleus (which grows spontaneously) requires a high surface energy related to the formation of the crystal–solution interface. Thus, the energetic barrier is found from the total free energy of the embryo,  $\Delta F_i^*$  (Christian 1975):

$$\Delta F_i^* = i^* kT \ln(\beta) + 4(i^*)^{2/3} \gamma_{cl} \Omega^{2/3} \quad (3)$$

with  $i^*$  the number of molecules in a critical nucleus obtained at the maximum of  $\Delta F_i^*$ :

$$i^* = \left( \frac{8 \gamma_{cl} \Omega^{2/3}}{3 k T \ln(\beta)} \right)^3 \quad (4)$$

where  $k$  is the Boltzmann constant,  $T$  the temperature,  $\beta$  the supersaturation of the solution according to equation (2),  $\Omega$  the molar volume of the solid and  $\gamma_{cl}$  the crystal–liquid interfacial energy.

Figure 2 shows the relationship between the supersaturation necessary for nucleation,  $\beta$ , and the number of molecules in a critical nucleus,  $i^*$ , for different salts at a temperature of 10 °C according to equation (4). The number of molecules to form a critical nucleus of mirabilite or epsomite is much larger at each supersaturation (mainly owing to the effect of its larger crystal–liquid interfacial energy), which means that the nucleation of these salts is energetically more difficult and requires higher supersaturation of the solution. Thus, mirabilite and epsomite are potentially more damaging salts, according to Figure 2.

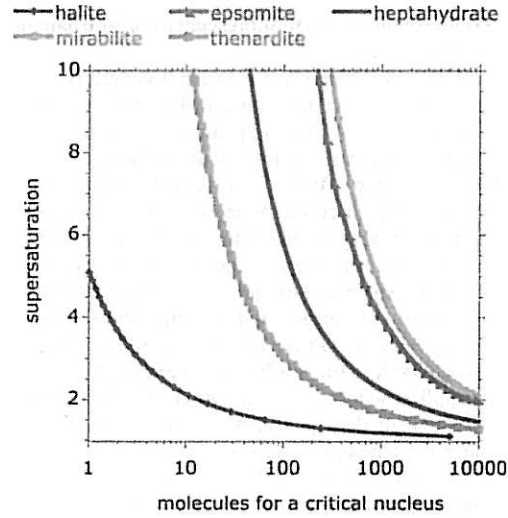


Fig. 2. Supersaturation of the solution for homogeneous nucleation of halite (NaCl), sodium sulphate heptahydrate ( $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ ), thenardite ( $\text{Na}_2\text{SO}_4$ ), mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) v. the number of molecules in a critical nucleus at 10 °C.

The presence of nucleation sites on the pore wall (impurities, defects or certain orientations of the mineral grains) decreases the energetic barrier and, consequently, the threshold supersaturation. In Espinosa-Marzal & Scherer (2008a), the threshold supersaturation for the nucleation of sodium sulphate heptahydrate and mirabilite in two different limestones is obtained by using differential scanning calorimetry (see the section on 'Methods of investigation'), and it confirms the tendency, predicted in Figure 2, of sodium sulphate heptahydrate to form at a lower supersaturation than mirabilite.

#### Drying – efflorescences, subflorescence and pore clogging

Salts may be carried into the stone with groundwater by capillary rise, or may be dissolved from the mortar joints, or result from chemical reaction between atmospheric pollutants (especially  $\text{SO}_2$ ) and minerals [such as calcite ( $\text{CaCO}_3$ ) in limestone]. As the water evaporates, the supersaturation of the pore solution increases until salt precipitates. A change in temperature, generally a decrease, leads also to a supersaturation of the solution resulting in the crystallization of salts. If evaporation occurs on the surface of the stone, then the crystals form a harmless (but unattractive) deposit on the surface called 'efflorescence'. However, if salts precipitate beneath the material surface (a phenomenon called

subflorescence or cryptoflorescence), severe damage can be induced.

Although efflorescence does not generally affect the coherence and endurance of building materials, it impairs the surface appearance, which can be significant in case of historical buildings. Indeed, there are some efforts to prevent the formation of efflorescence. For example, a penetrating sealer can help prevent or lessen the occurrence of efflorescence by soaking in and blocking the pores below the surface, thus preventing the water from moving to the surface and bringing the salts with it. However, this process might lead to the crystallization of salts some millimetres beneath the surface (as subflorescence) or even deeper, possibly causing more severe damage. Therefore it is important to understand the interaction between in-pore crystallization and moisture and salt transport, as well as how it may affect damage of the stone.

Whether efflorescence or subflorescence forms depends on the drying rate, which is strongly affected by the presence of salts. Initially, the evaporation takes place on the exterior surface, driven by the gradient of vapour pressure. Air penetrates first into the large pores. The liquid flow from the large into the small pores keeps the small pores filled with water, such that evaporation continues on the surface of the material; in the absence of salts, drying takes place at a constant rate (see Scherer 1995 for the general theory of drying).

The drying rate,  $m_d$ , is directly proportional to the gradient of the vapour pressure of the surrounding air,  $p_a$ , and of the boundary layer of vapour on the drying surface,  $p_s$ :

$$m_d = k_v(p_s - p_a). \quad (5)$$

The dissolved salts decrease the water activity, which decreases the pressure gradient in the vapour phase and, thus, the evaporation rate. This effect depends on the particular salt and is more significant with increasing supersaturation of the solution. For example, for  $\text{Na}_2\text{SO}_4$ , at a concentration of  $3 \text{ mol kg}^{-1}$  and  $20^\circ\text{C}$ , the water activity is  $a_w = 0.898$  and therefore  $p_s$  is smaller than that of pure water ( $a_w = 1$  in absence of salts). Thus, at 50% relative humidity and neglecting the temperature difference between the air and the surface, the estimated decrease of the evaporation rate is 20%. This effect and the decrease in the area of the drying surface by efflorescence (Sghaier & Prat 2009) are the reasons for the lack of a period of constant evaporation rate in the presence of salts.

During the initial period of decreasing drying rate, the meniscus penetrates progressively into smaller pores. As long as a continuous liquid film covers the pore walls from the meniscus up to the exterior surface, then liquid transport can proceed

by flow of the film, causing evaporation to take place on the surface and forming efflorescence. At the same time some liquid evaporates within the unsaturated pores, which causes salt to precipitate as subflorescence.

The decrease in the moisture content, the pore clogging with crystals and the increase of the solution viscosity with concentration may retard the liquid (capillary) flow. If the capillary flow becomes slower than the evaporation rate then the film becomes discontinuous and the flow to the surface is partly interrupted. Thereafter, evaporation takes place only inside of the material, indicating the start of the second (more accentuated) decreasing rate period of drying. As shown by Espinosa-Marzal & Scherer (2008b), at  $21^\circ\text{C}$  and 30% relative humidity (RH) for Indiana limestone the first decreasing drying period is of short duration in the presence of salt; it vanishes completely in the case of  $\text{MgSO}_4$ , mainly because of the slow advective flow due to the high viscosity of the solution. This also explains the absence of efflorescence of magnesium sulphate salts in this experiment.

The vapour transfer from the stone surface to the surrounding air is affected by efflorescence. In addition, liquid transport through the efflorescence is affected by its porosity or by the presence of a film. One can imagine that if efflorescence forms and impedes the capillary flow to the surface, but the drying rate remains high because the efflorescence permits diffusion of vapour, the drying front may move deeper into the material.

Recently, the effect of salts on the drying rate has been studied in limestone (Espinosa-Marzal & Scherer 2008b, 2010b). Salts lead to a significant decrease of the drying rate. The intensity of pore clogging was investigated through the uptake of decane by salt-contaminated samples. Very effective pore clogging is caused by sodium chloride (halite) and magnesium sulphate (epsomite/hexahydrate). Experiments show that the drying rate is strongly dependent on the type and amount of salt, and on the porosity of the substrate.

It is not understood yet whether pore clogging can enhance or retard damage. Thus, it can be expected that pore clogging close to the surface may reduce the evaporation rate and, thereby, prevent the solution from achieving high supersaturation within the stone. However, if pore clogging occurs within the drying front, evaporation might lead to supersaturation of the residual solution, which is present as a thin film between the crystals, and between the salt and the pore wall (Scherer 2004). As crystal growth cannot continue owing to spatial confinement, an increase of the crystallization pressure might be induced. The same effect could result from a decrease in the temperature. Moreover, the hydraulic pressure caused by the freezing of



water in pores whose entrances are clogged with salt crystals might cause significant damage. Thus, there are still important unanswered questions regarding pore clogging by salt crystals that should be the subject of future research.

In summary, the formation of either efflorescence or subflorescence, as well as the effectiveness of the pore clogging, depends on porosity of the stone, solution properties, nucleation and crystal growth kinetics, as well as on the environmental conditions. The only way to consider the interactions between all of these factors and to make a rough estimation of their effects is by means of numerical simulation.

#### *Numerical models for salt crystallization coupled with transport in porous stone*

Prediction of the position of the crystallization front under real climatic conditions requires the coupled heat, moisture and salt transport through the pore network to be analysed, together with the processes of phase changes of salts in the pores and chemical reactions (e.g. dissolution of carbonate rocks). From the point of view of comparing the behaviour of different salts, porous materials or the effects of diverse climatic conditions, the development of such numerical models is of interest for practical applications. Currently, there are several efforts to simulate these phenomena in porous building materials using models based on physical principles or empirical formulas (Černý *et al.* 2007; Franke *et al.* 2007; Nicolai 2007; Derluyn *et al.* 2008).

The coupled advective–diffusive partial differential equations for the transport of moisture and dissolved substances in porous media (Bear 1972), or its extended version including migration in an electric field based on the Nernst–Planck model (Samson & Marchand 1999), are well known.

The thermodynamics of salt solutions are also well known for the salts of interest in salt weathering. With the help of the Pitzer parameterization (Pitzer 1991; Steiger *et al.* 2008) it is possible to determine solution density, activity coefficients, supersaturation ratio (also of metastable salts: Steiger & Asmussen 2008), enthalpy of dissolution and specific heat capacity of solutions very accurately. This thermodynamic model permits prediction of which salts can precipitate from a solution consisting of an ion mixture at a given temperature, relative humidity and concentration; evidently, this may be of interest for assessing the cause of damage of particular sites.

In contrast, the kinetics of in-pore crystallization and the interaction between salt and substrate (pore surface) are not completely understood. For example, it is unclear whether the interfacial

energy might influence where crystals form (at the solid–liquid or liquid–air interface) according to Rodríguez-Navarro & Doehne (1999) and Shahidzadeh-Bonn *et al.* (2008) or in which pores the crystals will form preferentially in non-equilibrium conditions.

Recent publications accentuate the significant role of the kinetics of crystallization on the damage mechanism (Scherer 2004; Steiger 2005a, b; Espinosa *et al.* 2008a; Espinosa-Marzal & Scherer 2008a, 2010a; Espinosa-Marzal *et al.* 2010) and especially emphasize the role of the supersaturation of the solution. Rodríguez-Navarro & Doehne (1999) carried out evaporation experiments at 60 and 35% RH, respectively, with an environmental scanning electron microscope (ESEM). Depending on the evaporation rate, they observed several different phases including mirabilite, both anhydrous forms (Rodríguez-Navarro *et al.* 2000a) and, eventually, the heptahydrate (Rodríguez-Navarro & Doehne 1999), apparently dependent on the supersaturation ratio achieved.

Espinosa *et al.* (2008b) investigated the phase change of salts (crystallization, dissolution, hydration, dehydration and deliquescence) in capillary porous materials and used a diffusion–reaction model (Nielsen 1984) to calculate the average crystallization rate of salts in porous materials,  $S$ , according to:

$$S = K(\beta - 1)^g \quad \text{with } \beta > \beta^* \quad (6)$$

where  $K$  and  $g$  are kinetic parameters, and  $\beta^*$  is the necessary supersaturation required for crystallization to start. This equation is based on the fact that the driving force for crystallization is the supersaturation ratio of the solution with respect to a salt,  $\beta$  (Nielsen 1984). Three kinetic parameters are necessary to calculate the crystallization rate ( $K$ ,  $g$ ,  $\beta^*$ ), which generally depend on both pore surface and salt, and must be obtained experimentally for each salt–substrate combination. The starting supersaturation ratio gives the threshold condition for the phase change. If salts are already present in a pore, the threshold supersaturation for further crystallization becomes  $\beta = 1$ .

The following example shows how numerical simulation can help the damage mechanism of salt crystallization to be better understood. A capillary rise experiment of sodium sulphate in two bricks (A and B) of different porosity was performed in the laboratory at 50% RH and 23 °C (Espinosa-Marzal *et al.* 2008), and showed completely different behaviour for the two materials. While severe efflorescence formed in brick A, it was negligible in brick B even after 2 weeks. In contrast damage (flaking) was only observed in brick B.

A significant difference between the materials is the presence of large pores (*c.* 10  $\mu\text{m}$ ) in brick A, while most of the pores in brick B are smaller than 2  $\mu\text{m}$ . Thus, the measured sorptivity of brick A is approximately 3 times larger than that of brick B:  $S_A = 1.71 \text{ g}^2 \text{ s}^{-1}$  and  $S_B = 0.57 \text{ g}^2 \text{ s}^{-1}$ . For the crystallization rate of mirabilite equation (6) was applied. The kinetic parameters for the crystallization of mirabilite in this brick according to equation (6) were determined experimentally elsewhere (Espinosa *et al.* 2008b).

The numerical simulation of this laboratory experiment shows that the higher permeability and larger pores of brick A are responsible for low pore blocking and rapid transport of the solution to the surface forming efflorescence. Figure 3 shows the distribution of mirabilite in brick B computed with the engineering tool ASTra (Franke *et al.* 2007). Owing to the axisymmetric geometry, the simulation of the coupled transport with crystallization was performed in only half of the sample (cross-hatched surface in inset). Thus, the *x*-axis goes from 0 to 3 cm, the *y*-axis goes along the height of the sample (14 cm) and the computed mirabilite content is depicted on the *z*-axis. The bottom 4 cm of the sample is placed inside the pan, which

contains the unsaturated solution that keeps the relative humidity constant at 95%. Therefore, the evaporation inside of the container is negligible and no crystallization takes place. Above this 4 cm, mirabilite precipitates. The predicted width of the crystallization front is about 0.8 cm and no appreciable efflorescence forms, according to the simulation. The pores on the sample surface (at *x* = 0.03 m) contain salt crystals (*c.* 15 wt%) but there is no growth out of the pores (see arrow). Thus, the simulation with ASTra predicts just the formation of subflorescence, which is in agreement with the experimental results.

Espinosa *et al.* (2008b) show how the crystallization rate affects the results of the simulation. Thus, if a slower crystallization of mirabilite in brick B is assumed for the simulation, both the total amount of salt and the evaporation rate are larger, and so the damage more intense. The reason for this is simply the reduction in the number of crystals on the surface during the first stage of drying as a result of the lower crystallization rate, which leads to a smaller reduction in the evaporation rate as pore clogging is less effective. Because the evaporation rate is raised relative to the capillary transport rate, the crystallization front moves into the interior

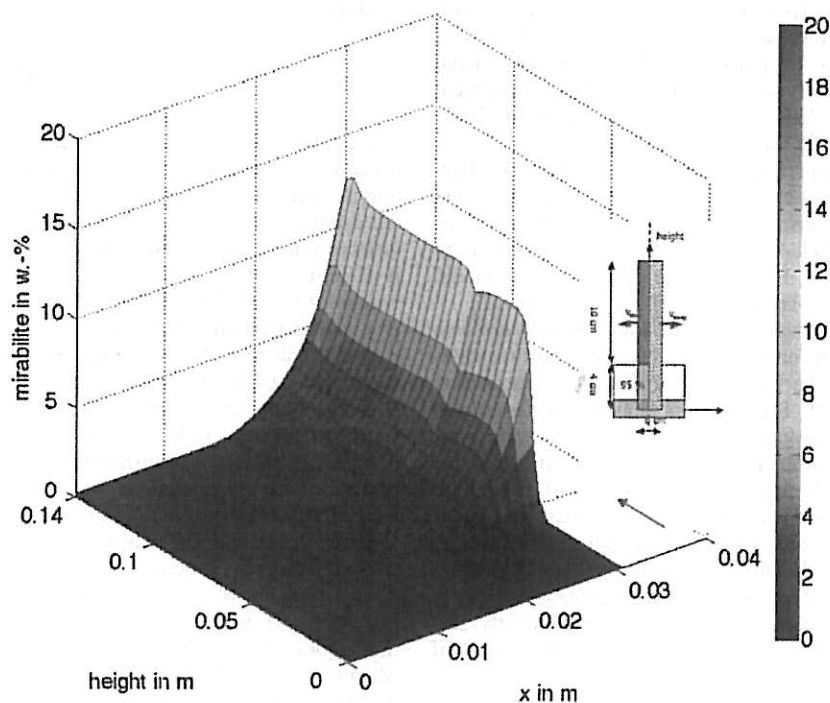


Fig. 3. Computed distribution of the content of mirabilite (in wt%) in brick B during the capillary-rise experiment after 196 h. Owing to the axisymmetric geometry, the simulation was performed on half of the sample (cross-hatched surface in inset). Simulations were performed with the engineering tool ASTra (Franke *et al.* 2007).

of the sample. As a result of the lower crystallization rate, the width of the crystallization zone reaches approximately 1.8 cm beneath the surface.

This example shows how a numerical simulation can help in the understanding of the interaction between mechanisms under particular boundary conditions. However, the applicability of the computational models is still restricted to specific scenarios.

### Crystallization pressure

Crystallization pressure is the main reason for the damage caused by the crystallization of salts in a supersaturated solution (Chatterji & Jensen 1989; Flatt 2002; Rodriguez-Navarro *et al.* 2002; Scherer 2004; Steiger 2005a, b). Correns (1949) (see also the annotated translation by Flatt *et al.* 2007) measured the growth pressure of a crystal against a load, and derived an expression for the crystallization pressure as a function of the supersaturation ratio by assuming that a thin layer of aqueous solution always remains between the crystal and the internal solid walls of the porous network, providing for the diffusion of the ions to the growing surface.

This concept can also be applied to a crystal growing in a pore: the growth of the crystal in a pore is impeded by the pore wall, but the crystal remains in contact with a supersaturated solution, at least temporarily. The reason for the formation of the thin film is the action of repulsive forces (i.e. disjoining pressure) between the two approaching solid surfaces (viz. the growing crystal and the pore wall). If this thin layer did not exist the crystal would come into contact with the pore wall, the growth would stop and no crystallization pressure would be exerted. Therefore, the existence of this thin layer is a necessary condition for crystallization pressure.

From thermodynamics it follows that a crystallization pressure,  $\Delta p$ , must be exerted to maintain a crystal in equilibrium in a supersaturated solution. According to Flatt (2002), Scherer (2004) and Steiger (2005a, b) the crystallization pressure is given by:

$$\Delta p = \frac{RT}{V_c} \ln \beta - \gamma_{cl} \kappa_{cl} + \frac{\Delta V}{V_c} \gamma_{lv} \kappa_{lv} \quad (7)$$

where  $\Delta V = V_L - V_c$ ,  $V_L = \sum V_i$  is the sum of molar volumes,  $V_c$  the molar volume of crystal,  $\kappa_{cl}$  the curvature of the interface between crystal and solution,  $\kappa_{lv}$  the curvature between liquid and vapour,  $\gamma_{cl}$  the crystal–solution surface energy and  $\gamma_{lv}$  the vapour–solution surface energy. The influence of the capillary pressure (the third term in equation 7) on the solubility and on the

crystallization pressure is relevant only in unsaturated porous materials.

The influence of the crystal curvature (given by the second term in equation 7) on the crystallization pressure must be considered in small pores. For example, if the threshold supersaturation for the nucleation of a salt is equal to 2, then the influence of the curvature is only relevant in pores with entries smaller than 12 nm. If the material contains such small pores, then a crystallization pressure can be expected in equilibrium (Scherer 2004; Steiger 2005b). Thus, for a cylindrical crystal with hemispherical ends in a cylindrical pore, if the solution is in equilibrium with the hemispherical surface of the crystal it is supersaturated with respect to the cylindrical surface and equation (7) reduces to:

$$\Delta p^\infty = \gamma_{cl}(\kappa_1 - \kappa_2) \quad (8)$$

where  $\kappa_1$  and  $\kappa_2$  are the curvatures of the cylindrical side ( $1/R$ ) and of the hemispherical ends ( $2/R$ ), respectively, and  $R$  is the pore radius. According to this, in a material with a bimodal pore size distribution, with  $R_2 = 1 \mu\text{m}$  and  $R_1 = 10 \text{ nm}$ , confined mirabilite would exert 7.96 MPa (assuming  $\gamma_{cl} = 0.04 \text{ N m}^{-1}$ ,  $\kappa_2 = 1/R_2$  and  $\kappa_1 = 2/R_1$ ).

In a non-equilibrium state, even in the absence of small pores, high mechanical stresses may arise owing to high supersaturation ratios, according to the first term in equation (7). That is, crystals come into contact with the pore walls while the solution is highly supersaturated, and they exert force on the wall until equilibrium is established (Scherer 2004; Espinosa *et al.* 2008a; Steiger & Anmussen 2008). At equilibrium, the large pores are filled with a saturated solution and stress-free crystals. A local increase in supersaturation ratio in the pores must be reduced by ion diffusion or solution transport; if these processes are slow, mechanical stress can be exerted over a considerable period of time and even cause material damage. This was proved experimentally for Indiana Limestone and Cordova Cream Limestone (which do not contain small pores) during the crystallization of sodium sulphate salts (Espinosa-Marzal & Scherer 2008a).

Indeed, the magnitude of the local supersaturation during the crystallization process depends on the dynamic interaction between nucleation and growth kinetics of each single crystal and the ion transport rates between connected pores, as well as on temperature. This is relevant for the prediction and prevention of damage, and therefore it should be an important field of future research.

Hydrostatic pressure from the change in volume has also been considered to be a reason for damage caused by salt crystallization (Correns 1949).

Certainly there is an increase in the total volume consisting of solution and salt crystals compared to the volume of the supersaturated solution before crystallization occurs. For example, when cooling a sodium sulphate solution with an initial concentration of  $3.34 \text{ mol kg}^{-1}$  from  $27^\circ\text{C}$  down to  $0^\circ\text{C}$ , a maximal volume increase of 3% is measured (Haynes 2006). However, the pore system is only partially filled with solution in practice and, consequently, the hydrostatic pressure can be simply released by pushing the solution into the empty pores without generating stress in the material. However, it cannot be excluded that hydraulic pressure becomes relevant in the presence of pore clogging or when ice and salt crystals (cryohydrates) form in the pore system simultaneously.

### Stress

The crystallization pressure causes a compressive radial stress on the pore wall and this is accompanied by a tensile hoop stress in the material (Scherer 1999). The net tensile stress, which is reflected in the expansion of the body during crystallization, can cause damage.

There are several comparative studies of salt damage in porous materials in the literature (e.g. Scherer 2004; Coussy 2006; Lubelli & van Hees 2007; Espinosa *et al.* 2008a; Espinosa-Marzal *et al.* 2008). According to equation (8), materials with smaller pores are more susceptible to salt damage, which has been confirmed experimentally (e.g. in Espinosa *et al.* 2008a; Espinosa-Marzal & Scherer 2008a; Espinosa-Marzal *et al.* 2009). The stress induced in the material depends on both pore size and salt distribution within the pore network, since these factors control the area over which the crystallization pressure is exerted.

According to equilibrium thermodynamics salt precipitates preferentially in large pores ( $>0.1 \mu\text{m}$ ), which constitute most of the pore volume of limestone. However, Espinosa-Marzal & Scherer (2008a, 2009a) give evidence that a non-equilibrium state is responsible for the high stress and damage induced by salt crystallization in stone with large pores. Since the salt distribution depends on various kinetic factors, there is no universal salt distribution. Efforts to characterize the salt distribution have been made; for example, by using mercury intrusion porosimetry. This method requires a severe drying of the sample, which may modify the original salt distribution by inducing solution transport or dehydration of the salt. Research is needed to examine the salt distribution using methods that do not require evaporation, such as freeze-drying, or *in situ* methods, such as nuclear magnetic resonance (NMR) (Pel *et al.* 2000) or radiography (Ketelaars 1995).

The stress exerted in a pore by a single crystal is not likely to generate cracking and failure of the body since the volume under stress is too small. Thus, for the stress generated by crystallization to act on the largest strength-limiting flaw in the material, the crystals must first propagate through a substantial volume of the pore space until its stress field reaches the flaw (Scherer 1999). A few attempts have been made to predict the average stress in the material. A good estimation can be obtained by multiplying the crystallization pressure by the fraction of the pore volume occupied by the crystals (Hamilton *et al.* 2008).

Poromechanics has been classically used to determine the deformation and the stress caused by pore pressure in saturated and unsaturated materials. The average stress results from a thermodynamically consistent overall elastic energy induced in the matrix by the pore pressure; damage is predicted when the average stress exceeds the tensile strength of the material. Recently it has been applied to problems of freezing in concrete (Coussy 2005; Sun & Scherer 2009) and of salt crystallization (Coussy 2006; Espinosa-Marzal & Scherer 2009a), and the estimations are very reasonable (see Cooling experiments in the section on 'Methods of investigation').

Another approach to predict damage is based on the existence of strength-limiting flaws in the stone. Thus, the tensile strength required to extend the flaw and cause failure can be determined according to fracture mechanics (Scherer 1999; Zehnder 2008). The application of finite-element method (FEM) simulations might help in detecting critical conditions for crack growth induced by salt crystallization.

### Methods of investigation

In the last two decades salt crystallization and capillary-rise tests have been widely applied to evaluate the resistance of stones to the damaging action of salt crystallization. We start this section with a short overview of the classical tests and describe briefly recent modifications that provide additional information. The second part of this section deals with experimental methods [such as pore-clogging and warping tests, differential scanning calorimetry (DSC) and differential mechanical analyser (DMA)] that provide *quantitative* information on different aspects discussed in the previous section, such as supersaturation for nucleation, kinetics of in-pore crystallization, pore clogging, crystallization pressure and resulting deformation.

Several other analytical techniques have been used to understand the nature of the phase changes of salts in solution or in the porous material, such as environmental scanning electron microscopy



(SEM) (Rodríguez-Navarro & Doehne 1999; Ruiz-Agudo *et al.* 2007), environmental X-ray diffraction (XRD) (Genkinger & Putnis 2007; Steiger & Linnow 2008), nuclear magnetic resonance (NMR) (Rijniers *et al.* 2005), and, more recently, synchrotron measurements (Hamilton *et al.* 2008; Espinosa-Marzal *et al.* 2009) and atomic force microscopy (A. Hamilton pers. comm.). We do not describe these methods specifically in this section, but include the information obtained from them.

#### *Bursting test or salt crystallization test*

The salt crystallization, or bursting, test (RILEM 1980) has been widely used for assessing stone durability against salt weathering, even if the validity of this accelerated method is controversial due to the extremely aggressive crystallization conditions (Price 1996; Tsui *et al.* 2003). The test consists of impregnation–drying cycles using sodium sulphate. During the impregnation, an unsaturated sodium sulphate solution is adsorbed by cubes of stone at constant room temperature. By drying at high temperature ( $>60^{\circ}\text{C}$ ), thenardite precipitates in the pores of the stone. Environmental scanning electron microscopy (ESEM) observations by Rodríguez-Navarro *et al.* (2000a) show that, during the wetting of thenardite, thenardite first dissolves and then mirabilite precipitates from the solution.

As the dissolution of thenardite leads to a solution highly supersaturated with respect to mirabilite below  $32^{\circ}\text{C}$ , a high crystallization stress exerted by mirabilite can be expected. Tsui *et al.* (2003) showed that damage occurs during the impregnation at  $20^{\circ}\text{C}$  (where mirabilite is stable), but not at  $50^{\circ}\text{C}$  (where thenardite is stable). This demonstrates that during the bursting test any damage is linked to mirabilite precipitation that occurs during the wetting step.

More recently, Steiger & Asmussen (2008) performed a similar test with the difference that the impregnation took place only by capillary uptake of the solution through the bottom surface of the samples, and at  $27^{\circ}\text{C}$  to avoid the possible formation of heptahydrate. Their modified set-up allowed the length change of the sample to be monitored using a dilatometer and confirmed that, indeed, an expansion was caused during the rewetting by the crystallization of mirabilite. Thus, the bursting test confirms the influence of the supersaturation on the damage mechanism by salt crystallization.

#### *Capillary-rise experiment with simultaneous drying*

It is well known, from evaporation experiments under conditions of continuous capillary absorption

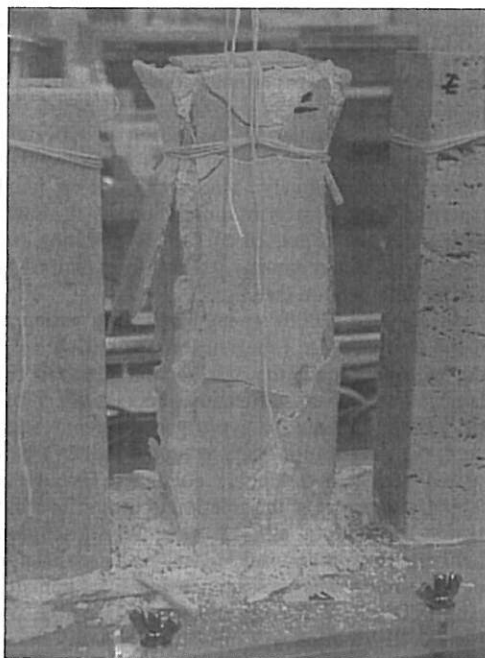


Fig. 4. Damage of Cordova Cream Limestone caused by the capillary-rise of an unsaturated sodium sulphate solution. The drying conditions are 34% RH and  $21^{\circ}\text{C}$ .

of an unsaturated solution, that crystal growth during evaporation can generate substantial stress leading to severe damage. This is illustrated in Figure 4 for Cordova Cream Limestone adsorbing sodium sulphate solution (12 wt%) and drying at  $22^{\circ}\text{C}$  and 34% RH (Scherer 2004). This experiment, introduced by Lewin (1982), simulates the penetration of salts with groundwater into stone or masonry in the field, while evaporation takes place on the surface. Thus, it includes the interaction between moisture and ion transport, environmental conditions and crystallization kinetics, which determine whether efflorescence or subflorescence forms in the field, as discussed in the previous section. However, the experiment fails to reproduce natural conditions in some important respects. First of all, the concentration of the salt solution is much greater in the laboratory than anything found in nature in order to accelerate the process. In addition, the samples are not subjected to the fluctuations in temperature and humidity that they would experience in nature, but this is necessary in order to have proper control of the experiment.

Sodium sulphate is most often used in the capillary-rise experiments, but sodium chloride was also used in Rodríguez-Navarro & Doehne (1999) and Espinosa-Marzal *et al.* (2008) and magnesium sulphate in Ruiz-Agudo *et al.* (2007). Both

sulphate salts are very often linked to severe damage under the conditions of this experiment.

Although this experiment does not allow a quantitative analysis of the damage, it offers the possibility of comparing the action of different salts, substrates and even of different preventive treatments qualitatively. Moreover, it is an ideal experiment for numerical simulation, as it allows analysis of the influence of factors affecting the crystallization and damage pattern, as explained in the previous section (see Fig. 3).

In Kiencke (2005) a very interesting variation of the capillary-rise experiment was used with the aim of determining the salt content required for damage owing to crystallization of potassium chloride, sodium sulphate and gypsum in different bricks. Here, the evaporation surface (upper surface) was treated with a hydrophobic coating to avoid the capillary transport of the solution to the surface and thereby preventing efflorescence. While solution uptake and evaporation take place, the length change of the sample was measured using a dilatometer gauge placed on the upper surface (see Fig. 5). The salt distribution was measured by X-ray fluorescence (XRF) and showed an enrichment of the precipitated salt just below the *c.* 2 mm coating depth, concentrated within a crystallization front approximately 1 mm thick. Thus, with this method it was possible to link damage with the salt content within the crystallization front or *critical salt content*.

#### Pore-clogging test

Pore clogging results from the interaction between in-pore crystallization and transport processes. A first attempt to evaluate the pore clogging induced by different salts in limestone has been made by Espinosa-Marzal & Scherer (2008*b*). The test consists of an initial impregnation of prismatic specimens ( $5 \times 2.5 \times 2.5$  cm) with an unsaturated

solution under atmospheric pressure. In this work NaCl ( $3.2$  and  $5.8 \text{ mol kg}^{-1}$ ),  $\text{Na}_2\text{SO}_4$  ( $0.85 \text{ mol kg}^{-1}$ ) and  $\text{MgSO}_4$  ( $1.68 \text{ mol kg}^{-1}$ ) were used. After impregnation five surfaces were coated with a special epoxy that seals wet surfaces to allow drying to occur through only one surface. Drying at  $31 \pm 2\%$  RH and  $21 \pm 1^\circ\text{C}$  took place over months. While reference samples impregnated with water were dry after 2 weeks, the presence of salt induced a significant slowing of the drying. After the samples reached constant weight, a sorptivity test was performed in which decane was absorbed through the only uncoated surface. Decane does not dissolve the precipitated salt and, consequently, comparison of the decane uptake before and after drying allows the resistance to the uptake caused by pore clogging with salt crystals to be compared. In Indiana Limestone, halite and magnesium sulphate salts lead to the highest pore clogging, while less intensive pore clogging was obtained with sodium sulphate salts, mainly due to the enhanced formation of efflorescence of thenardite. To determine the depth of the crystallization front and the pore filling within the crystallization front, the method developed by Hall & Hoff (2002) to calculate the sorptivity of a bilayer composite can be applied (work in progress).

#### Cooling experiments

The objective of the cooling experiments was to study nucleation and crystallization kinetics of salts in the porous material, as well as the induced stress. Crystallization of salts can be caused by cooling (or, in a few cases, heating) the solution, if the solubility is strongly dependent on temperature. For such salts the nucleation temperature (i.e. where the supersaturation threshold is reached) can be determined by differential scanning calorimetry, as crystallization is an exothermic (or endothermic) process. The threshold supersaturation gives an indication of the damaging nature of the salt because it is directly related to the crystallization pressure. The crystallization rate in the porous material can also be obtained, provided that the crystallization enthalpy is known (Espinosa-Marzal & Scherer 2008*a*). This technique permits comparison of the catalytic influence of different porous materials or the efficiency of nucleation inhibitors, among other things.

Some salts (notably including sodium sulphate and magnesium sulphate) can precipitate as different metastable or stable hydrated phases. For example, the concentration of the sodium sulphate solution (*in vitro* and in the pores of limestone), measured using NMR (Rijniers *et al.* 2005) as well as synchrotron X-ray analysis by Hamilton *et al.* (2008), indicates that the metastable sodium

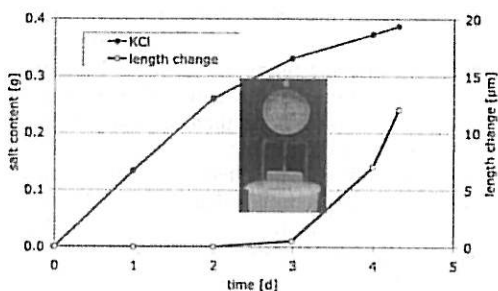


Fig. 5. Salt content in a brick ( $4 \times 4 \times 4$  cm) and measured length change during the capillary uptake and simultaneous evaporation of a potassium chloride solution over 5 days.

sulphate heptahydrate always forms prior to mirabilite when cooling down the solution. This has consequences from the point of view of stress because the crystallization of heptahydrate reduces the concentration and, consequently, the crystallization pressure that mirabilite can exert.

Espinosa-Marzal & Scherer (2008a) reported that the supersaturation required for the nucleation of mirabilite is much higher than that for heptahydrate, which suggests that mirabilite will be more damaging. This was confirmed with cooling experiments performed with the dynamic mechanical analyser (Espinosa-Marzal & Scherer 2008a, 2010a). Here, the expansion of different limestones saturated with sodium sulphate were measured during cooling-heating cycles. Damage was very often found to be related to the crystallization of mirabilite. Figure 6 shows the measured strain owing to the crystallization of both salts.

The expansion caused by heptahydrate starts at approximately 4 °C and remains during the isothermal hold ( $c. 60 \mu\text{m m}^{-1}$ ). After 600 min the rapid crystallization of mirabilite is responsible for the abrupt expansion, followed by a rapid relaxation and a much slower relaxation. The residual strain when heating up to 50 °C reveals damage of the limestone.

Using the theory of thermoporoelasticity (Coussy 2006), the crystallization pressure exerted by the precipitated salt, as well as the stress, can be estimated from the measured strain. Under the conditions of the cooling experiments, the crystallization pressure exerted by sodium sulphate heptahydrate is much smaller than that of mirabilite

(at 0 °C,  $\Delta p_{\text{hep}} \approx 11 \text{ MPa}$  and  $\Delta p_{\text{mir}} \approx 22 \text{ MPa}$ ). Moreover, the resulting stress induced by the crystallization of heptahydrate is not damaging, but it exceeds the tensile strength (3 MPa) of the stone during the crystallization of mirabilite (Espinosa-Marzal & Scherer 2010a). Similar values for the stress are estimated by multiplying the crystallization pressure (equation 7) by the fraction of the pore volume occupied by the crystals (Hamilton *et al.* 2008).

### Warping experiment

Warping of a stone-glass composite has been used to determine the deformation caused by the rewetting of samples containing thenardite, which induces crystallization of mirabilite (Espinosa-Marzal *et al.* 2010). A plate of glass is glued to a plate of thenardite-bearing stone; water or a salt solution is then allowed to wick into the stone, and the composite bends as crystallization pressure causes the stone to expand. Using a linear variable differential transformer (LVDT), the deflection of a limestone-glass composite (Indiana Limestone or Cordova Cream Limestone) was measured. Synchrotron radiation, producing hard X-rays, was used to examine the thenardite distribution in the initially dry sample and the kinetics of transformation to mirabilite on wetting. The warping results indicate that drying-induced crystallization of thenardite (in the oven at 105 °C) puts the stone into tension without causing any damage under the conditions of this experiment. The stress is relieved during the process of rewetting, when thenardite dissolves, as indicated by the initial positive deflection in Figure 7. Expansion is caused by the subsequent crystallization of mirabilite, which puts the stone plate again into tension and leads to the increasingly negative deflection in Figure 7.

To determine the stress related to the measured deflection of the glass-limestone composite during rewetting, the mechanical problem of bending was solved. This requires knowledge of the location of the advancing crystallization front of mirabilite, which is estimated by numerically modelling the solution transport coupled with sodium sulphate dissolution-recrystallization. Finally, the crystallization pressure exerted by the mirabilite crystals was obtained by applying poroelasticity theory. Thus, the estimated crystallization pressure exerted by mirabilite crystals is approximately 14 MPa at  $22 \pm 1$  °C. According to equation (7), the expected crystallization pressure under the conditions of this experiment is 12.8 MPa at 21 °C, considering that the maximal concentration of the solution is given by the solubility of thenardite at this temperature ( $3.69 \text{ mol kg}^{-1}$ ). The resulting stress depends on the amount of salt and on the pore-size distribution

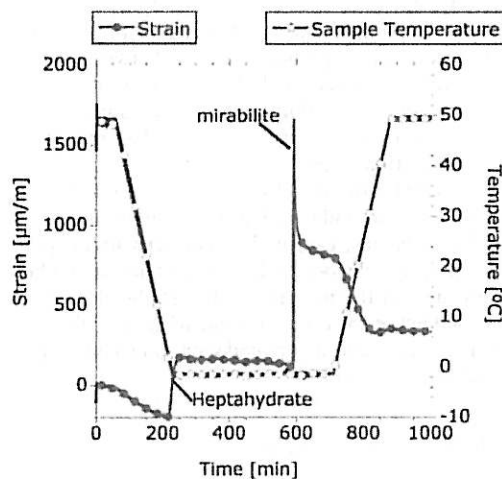


Fig. 6. Measured strain owing to crystallization and to thermal expansion/contraction of a sample of Cordova Cream Limestone impregnated with a sodium sulphate solution ( $2.9 \text{ mol kg}^{-1}$ ).

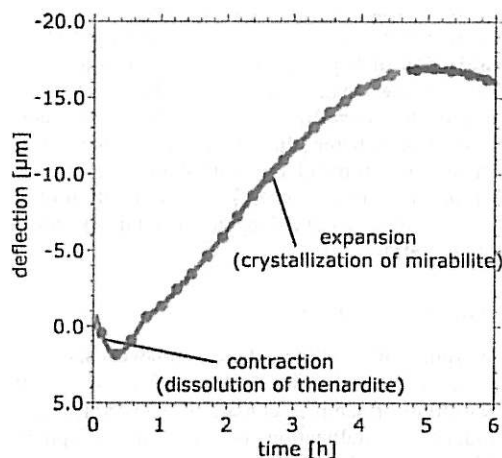


Fig. 7. Measured deflection during the rewetting of a sample of Indiana Limestone with sodium sulphate solution (20 wt%) at 20 °C in the warping experiment. A positive deflection indicates contraction of the stone plate, while a negative deflection corresponds to expansion.

of the material. Thus, the crystallization pressure is slightly overestimated by the model, but given the complexity of the coupled phenomena (transport, dissolution and crystallization) this result is reasonable.

In the previous sections it was shown that progress has been made in understanding the in-pore crystallization and the coupling with the transport processes; however, from a macroscopic point of view, there is still a lack of knowledge in a few aspects related to the *pore-level crystallization*. Thus, still an open question is the direct measurement of the crystallization pressure exerted by a crystal as it has not been possible to reproduce the Correns experiment so far (Flatt *et al.* 2007), except for ice (Buil & Aguirre-Puente 1981). There is indirect evidence that crystallization pressure can only be exerted if a thin film forms between crystal and pore surface, but the thin film has not been measured directly for salt, although it has been measured for ice (Wilen & Dash 1995). The interaction forces between the minerals of the substrate and the crystal, as well as the transport processes in the thin film, have not been quantified. The disjoining pressure could be addressed using atomic force microscopy or the surface force apparatus, and the mobility in the film could, perhaps, be measured using NMR, and these phenomena could all be simulated using molecular dynamics.

ESEM has provided important information by allowing direct observation of crystallization in a pore (see, for example, Rodríguez-Navarro & Doehne 1999). Determining the pore-size-dependent

salt distribution and dynamic redistribution in connected pores exceeds the current resolution of the ESEM. In contrast, NMR might help to visualize the pore-size-dependent crystal distribution (L. Pel pers. comm.), but it has not been carried out to date.

The propagation of cracks induced by the tensile stress involved in the crystallization process has not been studied in detail. Rapidly increasing computational power, however, may permit FEM models to simulate cracking induced by salt crystallization at the pore level.

Another important subject of investigation and debate deals with the control of nucleation, crystal growth and crystallization pressure to prevent damage from salt. This is discussed in detail in the next section.

### Methods for prevention

Methods that have been used to prevent or retard stone decay caused by salt crystallization include cleaning, desalination (poultices and methods based on electromigration), a variety of consolidants and surface coatings, such as water repellents, polymers to passivate the mineral surface and crystallization inhibitors (Price 1996). However, the effectiveness of these methods for the prevention of salt decay in porous materials is still controversial.

In the following discussion we focus on the additives that directly modify a step of the in-pore crystallization process (Füredi-Milhofer & Sarig 1996): nucleation (acting as inhibitor or promoter); crystal growth (as inhibitor of growth or modifier of the crystal habit); aging process, salt transport through the pore network (by modifying properties of the solution); and crystallization pressure (by changing the disjoining pressure between crystal and mineral surfaces). Indeed, there is no unique classification for additives as they usually affect rates and/or mechanisms of more than one of the crystallization steps.

Examples of crystallization additives with technological and industrial uses are phosphates and polyphosphates, carboxylic acid derivatives, polyelectrolytes, ferrocyanides, surfactants and phosphonates. In the present century studies have been carried out on the effect of some of them on the crystallization of salts associated with salt weathering of building materials.

### Modifier of nucleation

A crystallization or nucleation inhibitor causes salt to nucleate at a higher supersaturation. The purpose is to avoid crystallization by maintaining the salt dissolved in the solution until it is carried to the surface, where it precipitates as harmless



efflorescence instead of damaging subflorescence. However, there are several problems associated with nucleation or crystallization inhibitors.

- If crystallization takes place inside the stone, higher crystallization pressure will be exerted as a consequence of the higher supersaturation, and therefore more severe damage might be caused.
- The expected transport of the solution to the surface might be affected by several factors that are not accounted for. Thus, blocking of pores in the surface or a much more rapid evaporation rate (e.g. when submitted to extreme conditions of wind) might move the crystallization front into the stone.
- Currently, the capillary-rise experiment with simultaneous evaporation is used to determine the efficiency of inhibitors (and also of nucleation promoters). However, it cannot be excluded that the action of additives is dependent on the crystallization conditions. Rodríguez-Navarro *et al.* (2002) reported that one surfactant, a nucleation promoter, reduced damage during the capillary-rise experiment. However, after submerging the sample in water, the recrystallization of thenardite to mirabilite caused more severe damage in the treated stone than in the untreated stone.

Nucleation promoters catalyse the nucleation of salt so that it precipitates at a lower supersaturation. The effect of small quantities of borax as a nucleation promoter of mirabilite and of epsomite in biocalcaronite has recently been reported by Ruiz-Agudo *et al.* (2008). Here, the capillary-rise experiments clearly showed that the presence of borax in the absorbed solution is associated with a reduction in damage caused by salt crystallization and, therefore, it seems to be a promising method to prevent damage. It has to be remarked, though, that it might enhance pore clogging in some materials, the consequences of which are not yet predictable.

#### *Modifiers of crystal growth*

Some additives can either suppress or promote the growth of a crystal by adsorption on all its faces, whereas others act only on certain faces and thus also change the morphology of the crystal. The combination of ESEM and molecular modelling by Ruiz Agudo *et al.* (2006) shows that the most efficient growth inhibitors of mirabilite crystals among the studied phosphonates are those that display the best stereochemical matching with mirabilite surfaces. Classically, successful retardation of crystal growth was attributed to good matching between inhibitor and crystal interionic distance; however, the type, number and strength of the chemical bonds with the crystal surface seem to be

the determining factors (Füredi-Milhofer & Sarig 1996; Veintemillas-Verdaguer 1996). A different crystal habit leads to a different tensile stress owing to the different surface contact between the crystals and the pore.

#### *Modifiers of aging process*

There are multitudes of studies concerning the action of additives changing the aging process for industrial applications (Füredi-Milhofer & Sarig 1996). It is not obvious how an agglomeration process could cause more or less damage to stone. However, additives that could retard crystal aging by recrystallization from a metastable to a stable phase might be potentially interesting. Metastable salts are more soluble than stable salts and, consequently, they exert a lower crystallization pressure (Espinosa-Marzal & Scherer 2008a, 2010a). This has not been subjected to investigation in the field of salt weathering, but in other fields of material science, such as alloy casting (Magnin & Kurz 1988) or the pharmaceutical industry (Zhang *et al.* 2004), methods to promote the formation of metastable phases have been investigated to improve certain properties of the product. For example, we have shown that sodium sulphate heptahydrate exerts less stress on stone than mirabilite, so encouraging the formation of heptahydrate would appear to be beneficial; however, it is not clear that transformation of heptahydrate to mirabilite can be completely suppressed.

#### *Modifiers of solution properties*

Surfactants contain a hydrophobic part and a hydrophilic ionic group. They can adsorb on a crystalline surface through electrostatic interaction with the polar part (as the polyelectrolytes do), but further adsorption can take place at higher concentration due to hydrophobic interactions between their organic parts. Surfactants that lower the mineral-solution contact angle will enhance the capillary transport; this favours the formation of harmless efflorescence, preventing the formation of subflorescence. However, surfactants may also influence nucleation, and may induce significant morphological changes in crystallizing salts mostly due to preferential adsorption on particular crystal faces (Rodríguez-Navarro *et al.* 2000b). Therefore, it is necessary to study the effect of each surfactant on each particular salt before a reliable evaluation can be performed.

#### *Modifiers of disjoining pressure*

When a crystal grows from a supersaturated solution in a pore, a repulsive force (disjoining pressure) acts

between the two approaching surfaces, primarily resulting from electrostatic and solvation forces; in the case of ice, the van der Waals forces are also repulsive (Scherer 1999). As a consequence of the disjoining pressure, a gap between the crystal and the pore surface of approximately a few nanometres is filled by the solution. The existence of a supersaturated thin film is necessary for crystals to exert a pressure on the pore wall, as discussed before. Moreover, the disjoining pressure gives the maximal crystallization pressure that a salt crystal can exert on the confining surface. Atomic force microscopy allows measurement of the disjoining pressure in diverse research fields (e.g. in biomechanics) and is currently also applied to mineral-crystal interactions (Hamilton 2008 pers. comm.).

Indeed, if the crystal-stone interaction force was attractive, instead of repulsive, crystal and pore surface would come into contact and no thin film would form. The growth would stop and no pressure would be exerted. Based on this idea, additives capable of reducing the disjoining pressure or, ideally, converting repulsive into attractive forces might be very interesting from the point of view of preventing salt weathering, as proposed by Scherer *et al.* (2001). Houck & Scherer (2006) studied the behaviour of several polymers on the crystallization pressure. They argued that an effective polymer should be strongly adsorbed on the pore wall, and their ligands should be attracted to the surface of the salt crystal, allowing the pore wall to attract, rather than to repel, the salt. The result of the salt crystallization test on Indiana Limestone showed that polyacrylic acid, with a low molecular weight, offered the most protection against damage without changing the crystallization pattern and, consequently, its efficiency was associated with a decrease of the disjoining pressure. However, one of the problems associated with polyacrylic acid, and carboxylic acids in general, is its susceptibility to be washed out due to its weak binding to calcite. In addition, it is not known whether these polymers could also act as nucleation or crystallization inhibitors; if so, they might retard nucleation, but once crystallization starts the damage might be worse. Research is currently being carried out to clarify these questions.

Part of the complexity of the crystallization-additive interaction is the dependence of nucleation and crystal growth on the concentration of the additive, as well as on the additive-crystal mass ratio, as reported in Füredi-Milhofer & Sarig (1996). By increasing the additive concentration, an enhancement of nucleation is first observed; it reaches a maximum and then the trend reverses. The question is how to control the concentration in the field under changing climatic conditions. Moreover, temperature and pressure also alter

the effect of additives (Veintemillas-Verdaguer 1996). The effectiveness of these additives is also salt- and substrate-dependent (e.g. ferrocyanide in Rodriguez-Navarro *et al.* 2000b; Selwitz & Doehne 2002 and Lubelli & van Hees 2007; or diethylenetriaminepentakis methylphosphonic acid in Lubelli & van Hees 2007; Ruiz-Agudo *et al.* 2006). In the field we have to expect the presence of salt mixtures rather than of single salts. Therefore, laboratory work is required for each particular salt-substrate combination to assess the efficiency of the additive.

The application technique of such additives in the field is still in debate. Sprayed additives did not lead to satisfactory results in Lubelli & van Hees (2007). The application of additives by a poulticing technique might have bad consequences if salts dissolved and were transported deeper into the wall. Conversely, putting additives into the poultice might be favourable because it would allow salt to be sucked into the poultice without precipitating. Thus, the efficiency of this technique depends on the transport properties of the poultice, substrate and interface, and this has not yet been studied. Generally, desalination prior to the application of the additive seems advisable.

Currently a lot of effort is being invested to find proper additives, and progress is being made for specific applications in the laboratory. Of course, there will never be one universal treatment or one universal test to assess the reliability of each additive. Each site is subjected to particular conditions (environment, substrate porosity, salt mixture, presence of biofilm and swelling clays), so each site will require a skilled diagnosis before an appropriate treatment can be designed.

## Conclusions

This paper summarizes the main issues related to crystallization of salts in pores and the mechanisms of damage. The dynamic nature of the salt weathering process is emphasized through the accentuation of the influence of moisture and salt transport in the porous stone, crystallization kinetics, and the change in the pore structure by the clogging of pores with salts. Salt crystallization tests, capillary rise with simultaneous evaporation, cooling-induced crystallization and warping experiments are used to evaluate the damaging action of salts in stone, and to get quantitative information about crystallization kinetics and the induced deformation of the porous material.

Finally, an overview of the use of additives to reduce salt weathering is given. The philosophy of these additives is to decrease damage by altering a specific crystallization step (e.g. nucleation, growth), the solution properties or the disjoining

pressure. Laboratory experiments show that additives work successfully for specific scenarios, and therefore an accurate diagnosis and laboratory tests are required prior to the application of any treatment in the field. The capillary-rise test with evaporation and the salt crystallization test are used to determine the effectiveness of a treatment. Their efficiency under other crystallization conditions in the field is still questionable and therefore more effort is still necessary to understand better the dynamics of salt crystallization within the pore network, as well as the interaction with the additives.

This paper reviews the current state of salt weathering from a scientific point of view and indicates the questions that remain in debate. How does crystallization take place within a pore network? How do the processes in the thin film determine the crystallization pressure? Does pore clogging enhance damage? Can we modify the disjoining pressure? Can we control nucleation and crystal growth? Under what conditions does salt crystallization lead to crack propagation and failure of the material? Can we predict damage when salt mixtures or the combined action of salt and swelling clays are involved? By clarifying these questions, it will be possible to develop useful and practicable methods that can be applied to control salt damage in practice. Fortunately, research on these topics is progressing in many laboratories around the world, so the scientific foundation for protection of stone against salt crystallization is developing rapidly.

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